

Rec'd PCT/PTO 01 OCT 2004

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C03C 25/02, C08J 5/08	A1	(11) International Publication Number: WO 92/18431 (43) International Publication Date: 29 October 1992 (29.10.92)
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(21) International Application Number: PCT/US91/02499

(22) International Filing Date: 16 April 1991 (16.04.91)

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(81) Designated States: AT (European patent), BE (European patent), BR, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).

Published

With international search report.

(54) Title: A SIZE COMPOSITION FOR IMPREGNATING FILAMENT STRANDS

(57) Abstract

An aqueous size composition for glass fibers is disclosed which includes a thermoplastic polymer resin powder, a coupling agent, and fugitive processing aids, such as binders or film formers. The composition is applied to the glass fiber surfaces during the fiber forming process. A fugitive rheology modifier material may be added to the size composition. One embodiment of the composition includes a polyethylene oxide binder material and polyphenylene sulfide thermoplastic polymer resin.

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DESCRIPTIONA SIZE COMPOSITION FOR IMPREGNATING FILAMENT STRANDSTECHNICAL FIELD

15 This invention relates to a size composition useful for impregnating a highly loaded, impregnated fibrous strand where the impregnation takes place during the fiber forming operation. In one of its more specific aspects, this invention relates to a thermoplastic powder impregnated glass fiber strand.

20

BACKGROUND ART

25 The production of impregnated fibers and the application of thermoplastic resins to the fibers is well-known. Such fibers are coated with the thermoplastic resin after the fiber strand has been formed.

30 Sizing compositions typically employed as coatings for glass fibers have conventionally been applied to the surface of the glass fibers after the glass fiber has been formed. Typically it is necessary to first produce the glass fibers by providing a thin layer of a size composition to the surface of the bare glass fibers. The size composition must be compatible with the glass fiber and the resin which is subsequently applied to the sized fiber. The size composition serves to improve the bonding relationship between the glass fibers and the polymeric or thermoplastic resins. The glass fibers are then collected into a strand and the strand is wound around a take-up bobbin to form a substantially cylindrical package,

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5 conventionally termed a "yarn package". The yarn package is then
air dried or subjected to elevated temperatures in order to dry the
size composition applied to the surface of the glass fibers. The glass
fibers are thereafter impregnated with the thermoplastic resin to
form an impregnated yarn or cord.

10 However, it is difficult to produce a high performance
thermoplastic impregnated glass fiber strand. Normally, the size
composition include various processing aids which aid in improving
the bonding relationship between the thermoplastic resin and the
glass fibers. However, these processing aids remain in the
15 impregnated strand. The processing aids are undesirable materials
when clean thermoplastic impregnated glass fibers are desired, such
as for use in producing high performance thermoplastic impregnated
fibrous strand.

20 Considerable time and expense would be saved if a size
composition useful for impregnating strands with a thermoplastic
resin were available which could be applied during the fiber forming
process without the need for non-aqueous solvents, fluidized beds,
sheaths or time-consuming manufacturing processes.

25 Moreover, it would be beneficial if a size composition could be
employed which, when directly blended with the thermoplastic resin
during the glass fiber forming process, produces a substantially pure
thermoplastic impregnated glass strand.

DISCLOSURE OF INVENTION

30 According to the present invention, there is provided a slurry
composition for impregnating glass fibers which includes a
thermoplastic resin and fugitive processing aids such as a binder or
film former material and a thickening agent (or rheology modifier).
The slurry composition of the present invention includes the use of
35 fugitive processing components together with a non-fugitive polymer
to obtain a "prepreg" of the non-fugitive polymer. The slurry

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5 composition is applied to the glass fiber during the fiber forming operation. The composition of this invention can thus be applied as a size for glass fibers during the fiber forming operation and the resulting sized thermoplastic impregnated glass fibers can then be fabricated into glass fiber reinforced products.

10 According to the present invention, there is no need to first apply a sizing composition to the glass fibers and thereafter impregnate the resulting sized glass fibers with a compatible polymeric resin matrix in order to provide a thermoplastic reinforced fibrous strand. The slurry composition of the present invention provides a sized glass fiber impregnated with a compatible polymeric 15 resin matrix. The impregnated glass fiber is free of undesired processing materials and is therefore useful for various high performance glass reinforced end use items.

20 These and other aspects and advantages of the present invention will become clear after consideration is given to the detailed description of the invention which follows.

BRIEF DESCRIPTION OF DRAWINGS

25 Figure 1 is a graph showing the thermogravimetric analysis of a slurry containing polyphenylene sulfide.

Figure 2 is a graph showing the thermogravimetric analysis of a glass fiber impregnated with the slurry shown in Figure 1.

BEST MODE OF CARRYING OUT INVENTION

30 The present invention relates to a slurry composition useful for producing an improved yarn or strand (bundle of filaments) pre-impregnated with a thermoplastic polymer during the filament forming operation.

35 The present invention is compatible with any glass fiber conventionally utilized for the reinforcement of polymeric resins.

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5 The term "glass fibers" as used herein shall mean filaments formed by
attenuation of one or more streams of molten glass and to strands
formed when such glass fiber filaments are gathered together in the
forming process. The term shall also mean yarns and cords formed by
applying and/or twisting a multiplicity of strands together and to
woven and non-woven fabrics which are formed of such glass fiber
10 strands, yarns, or cords.

15 The individual components utilized in the practice of this
invention are commercially available and can thus be simply blended
with one another in the preparation of the formulation embodying the
features of the present invention.

15 Generally, the composition of this invention may contain a
carrier solvent, normally water, a coupling agent, and fugitive
processing aids such as a binder or film former material, a thickener
or rheology modifier material, and a matrix thermoplastic resin
powder dispersed in the sizing to form a slurry.

20 Any suitable coupling agent can be employed in the successful
practice of this invention. The coupling agent acts to produce
adhesion between the matrix resin and provide strength development
and retention of the matrix resin in the slurry. One example of a
25 suitable coupling agent is a silane such as a diamine silane (Z6020
from Dow Corning). The coupling agent can be contained in an
amount of about 1.2 percent, by weight, of the slurry mixture.

Any suitable fugitive binder material can be employed.
Alternatively, the fugitive thickener material may be the same
30 materials as the binder material. The binder or film former material
aids in the handling and processing of the filament during the fiber
forming process. Suitable binder or film former materials are, for
example, epoxy, polyester, polyvinyl acetate, polyvinyl alcohol,
acrylics, or other chemicals which have the ability to bond the
35 thermoplastic powder particles to the fiber upon the evaporation of
the water or which have the ability themselves to suspend the

5 particles in the slurry and subsequently bond themselves to the fiber.
One example of a suitable fugitive binder material is polyethylene
10 oxide. The binder material will be contained in an amount within the
range of from about 1.0 to about 1.2 percent, by weight, of the
slurry mixture.

10 Any suitable fugitive thickener material can be employed. The
thickener material acts as a rheology modifier so that the
thermoplastic powder particles will actually adhere to the fiber.
Without the thickener material the thermoplastic powder particles
15 may stay behind on the rolls of the applicator while the carrier
solvent goes on the fiber. The result would be a rapid build-up of
powder on the applicator rolls, which in turn, rapidly causes fiber
breakage.

20 The thermoplastic resins are dispersed into the sizing in the
form of fine particles. One example of a resin is polyphenylene
sulfide. In a preferred embodiment the size of the powder particles
are less than about 125 microns. According to the present invention
the resin powders can be applied to the filaments in an amount within
25 the range of between about 5 to about 50 percent, by weight, of
the final prepreg yarn or strand.

25 According to the present invention the sizing composition
suspends the thermoplastic powder particles in the slurry. The slurry
compositions of this invention are best produced by blending all
materials in their liquid state with agitation. A uniform coating of
the composition can be applied to the glass fibers in any suitable
30 manner during the fiber forming process. Preferably, the
compositions of the present invention are applied to the surface of
the glass fiber in the manner described in the co-pending U.S.
Application Serial No. 07/269,089, filed November 9, 1988 now U.S.
35 Patent No. _____, issued _____, which is a
continuation of Serial No. 07/024,953, filed March 12, 1984, now
abandoned, (the entire disclosure thereof being expressly

5 incorporated herein to by reference). The resultant slurry composition is sufficiently liquid to be applied to the fibers during the fiber-forming operation. Each fiber is coated by the slurry mixture as the fibers are formed, that is, at or about the place in their formation where the conventional size compositions are typically applied (e.g., between the bushing and the spindle on which 10 the fibers are wound as a package). In one fiber forming process, the continuous fibers leave the bushing and are dipped into the slurry and are impregnated with the slurry.

15 It is also within the contemplated scope of this invention that organic or inorganic particulates, such as metallic fillers useful in producing conductive rovings, may also be used with the thermoplastic polymer powder particles. These fillers can either be pre-combined with the polymer so that each powder particle contains polymer and filler or be added separately as a powder to the slurry.

20 The resultant impregnated strands can be chopped, either before or after drying, to be used for such operations as injection molding. Continuous thermoplastic impregnated strands can be filament wound or pultruded to achieve thermoplastic fiber reinforced end use items.

25 High performance thermoplastic resins exhibit advantages over thermosetting polymers when used as a matrix resin in fiber reinforced compositions. These advantages include better high temperature performance, better hydrolysis resistance, better impact properties, better electrical properties, better chemical resistance and better dielectric properties.

30 A convenient way to fabricate a fiber reinforced high performance thermoplastic is to use pre-impregnated thermoplastic strands. This is especially useful for high performance thermoplastic reinforced with continuous fibers. This invention describes such a 35 thermoplastic pre-impregnated strand.

5 A thermoplastic powder is dispersed in water. Usually, a
surfactant is added to the water to help wetting of the powder. A
thickener, usually a water soluble polymer, is added to build-up the
viscosity of the liquid phase. Other additives such as silane coupling
agents can also be added to the aqueous suspension (also called
"slurry"). This slurry is used as a size and applied to glass fibers as
10 they are being formed, as disclosed in the co-pending patent
application Serial No. 07/289,089, discussed above. The thickener is
chosen so that it is thermally decomposed into volatile products at a
temperature inferior to the decomposition temperature of the
15 thermoplastic powder and which is decomposed in the presence of
this thermoplastic, even after this thermoplastic has been fused,
without objectionally deteriorating the properties of this
thermoplastic. Examples of such thickeners include polyethylene
oxide, hydroxypropylcellulose, starch, and hydroxyethylcellulose.
20 This thickener may also be used as a "binder". The binder is used to
hold the thermoplastic powder on the strand of fibers upon drying,
and therefore providing an impregnated strand having good integrity.
Alternatively, the binder may be an additional ingredient added to
the slurry; however, the thickener chosen is also thermally
25 decomposable. The wetting agents chosen are also volatile or
thermally decomposable at an appropriate temperature.

Once the slurry is applied to the glass fiber, the forming
package is dried. Subsequently, the thermoplastic impregnated fiber
is heated to a temperature above the fusing temperature of the
30 thermoplastic powder so that the powder is totally or partially fused
or held to the fibers without having to rely on a binder. This heating
step may include, or be preceded by, partial decomposition of the
fugitive ingredients, thus, completing decomposition of the fugitive
ingredients at a temperature above or below the fusing temperature
35 of the thermoplastic. Any of these steps may be combined with
modification of the thermoplastic such as "curing" or "annealing".

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INDUSTRIAL APPLICABILITY

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EXAMPLE 1

10 A fine powder (<125 microns) of a high performance thermoplastic such as polyphenylene sulfide powder (Ryton VI from Phillipps Chem.) is dispersed in a water solution of a wetting agent in the following proportions: (parts by weight) 1200 parts water; 4 parts Tergitol Nin Foam 2 x (from Union Carbide) which are stirred together; add: 800 parts Ryton VI and stir until good wetting is achieved; add 14800 parts water and stir.

15 This slurry is poured in small quantities through a 115 mesh sieve to separate the powder into coarse and fine fractions. The slurry is passed through the sieve, collected and allowed to settle for at least 12 hours. The powder which has settled is collected by passing through 115 mesh. The liquid on top (later called water/surf) is also collected.

20 25 A slurry of the following composition is prepared: 1200 parts Ryton VI through 115 mesh (equivalent dry powder); 2764 parts water/surf; add 48 parts polyethylene oxide (Polyox WSR 205 from Union Carbide) mix well until homogeneous. This provides a slurry containing 31.1% solids. The glass fibers are coated as they are being formed with the slurry described above. The slurry is applied with a standard size applicator fitted with a doctor blade to control the film thickness on the applicator roll.

30 Two forming packages having 2000 filaments/strands are made as follows:

Package #1 total amount of solids on glass = 21.1%

Package #2 total amount of solids on glass = 20.0%

35 The package #1 is dried for one day at room conditions. The package (after substituting a steel for a cardboard forming tube) is

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5 then placed in an air oven at 300°C for 1 hour. The polyphenylene sulfide fuses, the polyoxyethylene oxide thermally decomposes into volatile matter and the polyphenylene oxide cures into a higher molecular weight polymer. When the package is removed from the oven and cooled, the strand of impregnated glass can be easily 10 unwound from the package inspite of the high amount of impregnating resin.

15 This strand is filament wound in a mold to form a unidirectional composite. The strands can then be compression molded into end use items. The measured flexural strength of 8014.2 kg/sq.cm. (114 k psi) indicates that the strand has useful mechanical properties.

20 15 Package #2 is dried in the same manner as package #1 but before fusing the polyphenylene sulfide the strand is wound onto a plate to form unidirectional layers. The plate is then placed in an oven at 300°C for 1 hour as was done for package #1 above. The unidirectional layers fuse into a sheet which can later be used for 25 compression molding unidirectional composites. The measured flexural strength is 8436 kg/sq.cm. (120,000 psi) which also indicates useful mechanical properties.

EXAMPLE 2

25 30 35 A fine powder (<125 microns) of a high performance thermoplastic such as polyphenylene sulfide powder (Ryton VI from Phillipps Chem.) is dispersed in a water solution of a wetting agent in the following proportions: (parts by weight) 1200 parts water; 4 parts Tergitol Nin Foam 2 x (from Union Carbide) add: 800 parts Ryton VI and stir until good wetting is achieved; add 14800 parts water and stir. This slurry is poured in small quantities through a 115 mesh sieve to separate the powder into coarse and fine fractions. The slurry is passed through the sieve, collected and allowed to settle for at least 12 hours. The powder which has settled is collected by passing through 115 mesh. The slurry of the following composition is

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5 prepared: 1200 parts Ryton VI through 115 mesh (equivalent dry powder); 2764 parts water/surf; add 42 parts polyethylene oxide (Polyox WSR 205 from Union Carbide) and 48 parts diamine silane (Z6020 from Dow Corning). This provides a slurry containing 31.8% solids. The glass fibers are coated as they are being formed with the slurry described above. The slurry is applied with a standard size applicator fitted with a doctor blade to control the film thickness on the applicator roll. A forming package having 2000 filaments/strands is made.

total amount of solids on glass = 26.2%

15 The package is dried for one day at room conditions. The strand is wound onto a plate to form unidirectional layers. The plate is then placed in an air oven at 300°C for 1 hour. The polyphenylene sulfide fuses, the polyoxyethylene oxide thermally decomposes into volatile matter and the polyphenylene sulfide cures into a higher molecular weight polymer. When the plate is removed from the oven 20 and cooled, the unidirectional layers fuse into a sheet which can be used for compression molding unidirectional composites. The measured flexural strength indicates useful mechanical properties: 10545 to 13357 kg/sq.cm. (150,000 to 190,000 psi) depending on molding conditions which indicates useful mechanical properties.

25 Thermogravimetric analysis (TGA), as shown in Figs. 1 and 2, confirms the removal of fugitive components through thermal degradation. In a first series of tests the sample is heated at a uniform rate of 20 degrees centigrade per minute and the sample weight is recorded as a function of temperature.

30 Figure 1 shows that pure polyphenylene sulfide (PPS) exhibits nearly no degradation below 300°C and very little loss weight up to 500°C. On the other hand, polyethylene oxide used as a fugitive thickener and binder starts to degrade at 200°C and has nearly completely volatilized by the time the temperature reaches 400°C.
35 The solid curve shows the weight loss of the dried slurry as the

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5 temperature increases. The weight loss from 200°C up to point A is
due to the loss of polyethylene oxide in the slurry. Above point A,
the loss in weight in the remaining PPS in the dried slurry is
essentially the same as the loss in weight in pure PPS.

10 In another thermogravimetric analysis shown in Fig. 2, glass
impregnated with the slurry described in example 1, and dried, is
suddenly exposed to a temperature of 300°C (to simulate the thermal
history of the dried impregnated glass placed in an oven at 300°C for
1 hour). The weight of the sample was followed. As can be seen in
Fig. 2, within 5 to 10 minutes, most of the volatile materials
15 thermally decomposed and the volatile materials have been removed.
After 1 hour there is no further weight loss. The recorded weight
loss of (100-98.2) = 1.8% is due to the loss of the polyethylene oxide,
a small amount of volatiles in PPS and residual moisture in the
strand.

20 While reference has been made to the preferred formulation in
accordance with the present invention, those skilled in this art may
recognize that various modifications may be made, which
modifications shall accorded the broadest scope of the appended
claims so as to encompass all equivalent formulations, compositions
25 and the like.

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10 CLAIMS:

1. A glass fiber at least a portion of the glass fiber's surfaces coated with the residue produced by evaporating water from an aqueous composition applied to the surface of the glass fiber during the formation of the glass fiber, the aqueous composition 15 consisting essentially of, in weight percent, based on the weight of the aqueous composition, about 30 to 50 percent, polyphenylene sulfide thermoplastic resin powder having an average particle size of about 125 microns or less, about 0.005 to 5.0 percent, diamine silane coupling agent, about 0.5 to 5.0 percent, polyethylene oxide thickener 20 material, and, a water surfactant.

2. A glass fiber at least a portion of the glass fiber's surfaces coated with the residue produced by evaporating water from an aqueous composition consisting of, in weight percent the 25 following: polyphenylene sulfide - 29.66 wt.%, polyethylene oxide - 1.04 wt. %, diamine silane - 1.18 wt. %, and, water surfactant - 68.18 wt. %.

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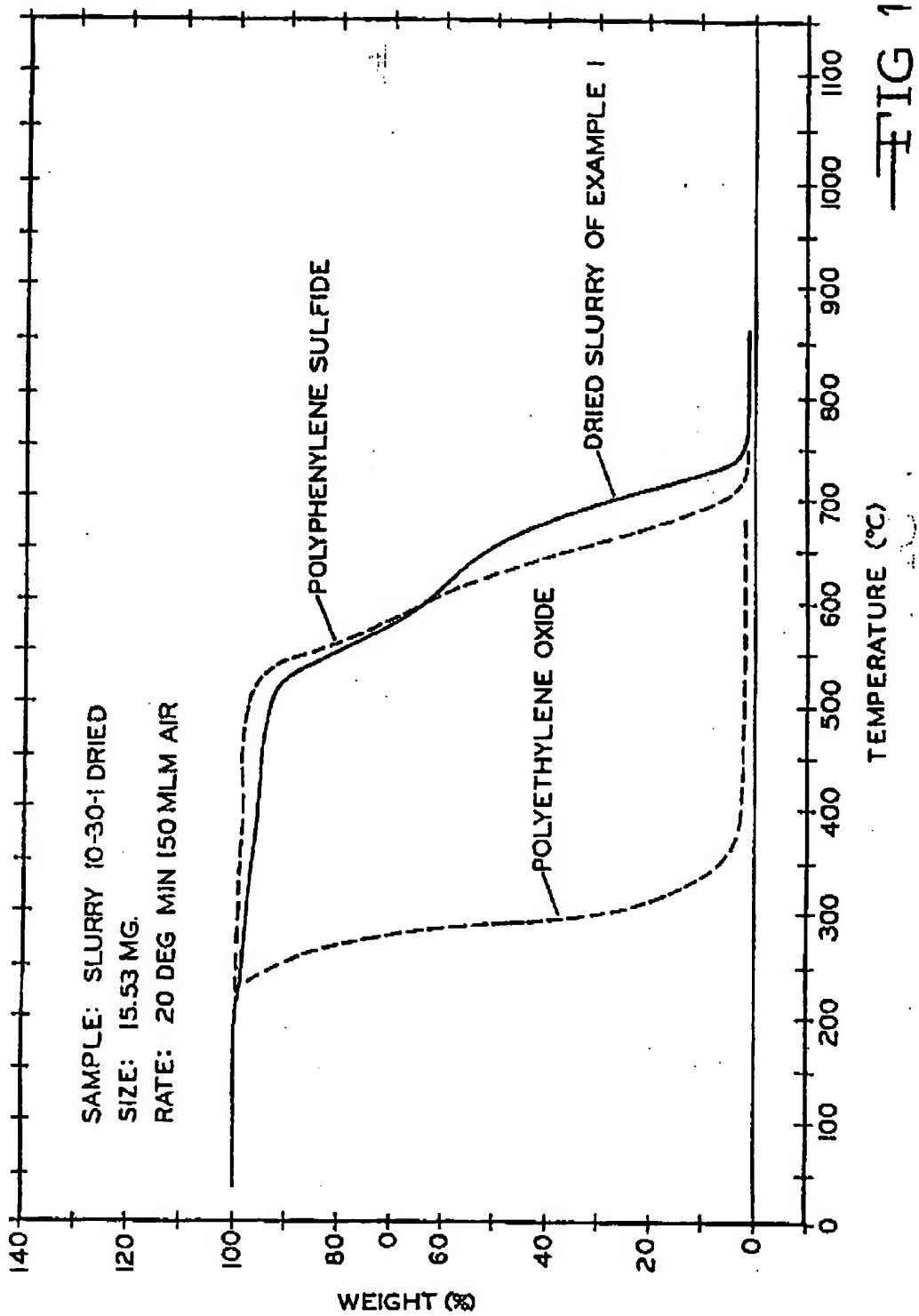
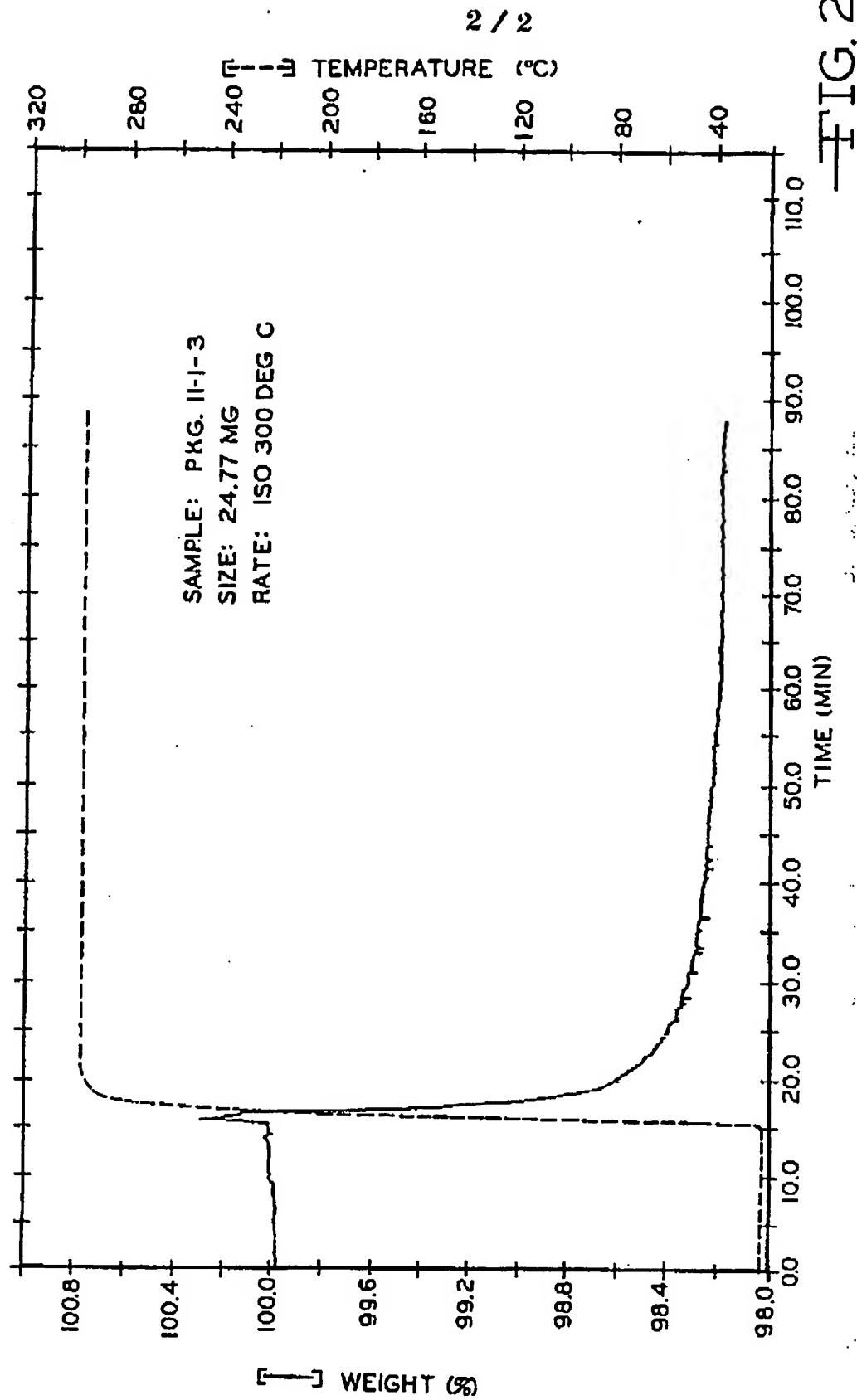


FIG 1

TGA



I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C03C25/02 ; C08J5/08

II. FIELDS SEARCHED

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Classification System	Classification Symbols	
Int.Cl. 5	C03C	;

Documentation Searched other than Minimum Documentation
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Category ¹⁰	Citation of Document, if with indication, where appropriate, of the relevant passages ¹¹	Relevant to Claim No. ¹²
A	GB,A,1264432 (HERCULES INCORPORATED) 23 February 1972 see page 2, line 2 - page 4, line 68 ---	1, 2
A	US,A,2778764 (MORRISON) 22 January 1957 see the whole document ---	1, 2
A	EP,A,58141 (KEMANORD AB) 18 August 1982 see page 2, line 1 - page 4, line 8 ---	1, 2
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IV. CERTIFICATION

Date of the Actual Completion of the International Search 05 JULY 1991	Date of Mailing of this International Search Report 18 JUL 1991
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer VAN BOMMEL L.

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A-1264432	23-02-72	DE-A- FR-A, B	2020813 2040319	05-11-70 22-01-71
US-A-2778764		None		
EP-A-58141	18-08-82	AU-A- CA-A- JP-C- JP-A- JP-B- SE-A- US-A-	7977382 1173200 1338469 57147523 61002692 8100819 4451585	04-11-82 21-08-84 29-09-86 11-09-82 27-01-86 06-08-82 29-05-84
US-A-3498826	03-03-70	BE-A- CH-B- DE-A- FR-A- GB-A- NL-A-	696231 561671 1669582 1517247 1176875 6704500	29-09-67 15-05-75 10-09-70 07-01-70 02-10-67

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